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The MEMOLED: Active Addressing with Passive Driving

*Kamal Asadi, Paul W. M. Blom, and Dago M. de Leeuw**

Organic light-emitting diodes[1] are emerging in the display market.[2] Monitors are already commercially available in mobile phones and small, ultrathin television screens. Images are produced by active matrix addressing using one or two transistors per pixel.[3] Light-emitting polymers have great potential for large area applications like signage, because they can be processed from solution.[4–6] The bottleneck that prevents realization of large light-emitting billboards is the driving scheme; a single transistor per pixel for signage applications is cost prohibitive.[7,8] It is acknowledged by industry "that the already large market for flat TVs would grow to atmospheric proportions if the cost decreases enough. The next horizon then would even include signage applications".[9] A big challenge is to simplify the driving scheme and to reduce the number of processing steps.[9,10] As a solution we here present a new device, the MEMOLED, an organic light-emitting diode with a built-in ferroelectric switch. The bistable diode can be programmed into a non-emissive off-state and a non-volatile emissive on-state. Static images are generated with a passive matrix driving scheme that can be scaled to large area.

To address the pixels in the display either passive- or active matrix driving schemes are used.[7] A passive matrix display contains a light-emitting layer sandwiched between two layers of perpendicular electrodes.[11,12] The individual pixels are addressed by applying appropriate pulses to the row and column electrodes. The technology is simple but limited to small displays with low resolution due to high power consumption and cross-talk between the pixels.[13,14] The limitations are lifted when using active matrix driving, where each pixel is addressed by a thin film transistor.[3] The bottleneck that presently prevents realization of large pixelated light-emitting billboards is the above mentioned driving scheme: a single transistor per pixel for signage applications is expensive and the cost superlinearly increases with the size of the display.[9,10] For signage applications such as large outdoor displays with low refresh rate there is as yet no solution.[9,10] The information cannot be displayed using a passive matrix and an active matrix is cost prohibitive.[7] Here we present the MEMOLED solution, an organic light-emitting diode with an integrated bistable, non-volatile programmable memory. The MEMOLED concept is based on a tuneable injection barrier, realized with a phase separated blend of a light-emitting polymer and a ferroelectric polymer. The polarization field of the ferroelectric is used to modulate the injection barrier at the semiconductor–metal contact, yielding an integrated on/off switch for light emission. Programmability of the integrated memory allows active addressing of the OLED in a passive matrix geometry.

The MEMOLED concept is depicted in **Figure 1**. We used poly(9,9-dioctylfluorenyl-2,7-diyl) end-capped with dimethylphenyl, commercially known as PFO, as a light-emitting polymer. Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of PFO amount to 5.9–6.1 eV and 2.9 eV respectively.[15,16] A random copolymer of poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) (ratio 80%–20%) was used as ferroelectric polymer. Chemical structures of the polymers are shown in Figure 1a. As anode a semi-transparent gold bottom electrode is used. Films spin-coated from a common solution phase separate yielding bi-continuous semiconducting PFO domains embedded in a P(VDF-TrFE) matrix. The MEMOLED is finished by evaporating the cathode, a thin layer of barium capped with aluminum.

The electrical properties of the individual components are preserved in the blend.[17] The ferroelectric polymer provides the non-volatile switching due to its bistable polarization response to the electric field, and the semiconducting polymer provides conduction and light emission. The operation mechanism is depicted in Figure 1b,c. The ferroelectric is a pure insulator, thus current can only flow through the semiconducting PFO phase. The barium/aluminum cathode is a good injecting contact for electrons, with a negligible injection barrier.[18,19] For hole injection into PFO, we deliberately used a gold anode. The work-function of the gold anode amounts to 4.7 eV as measured with a Kelvin probe. The injection barrier from gold into the HOMO of PFO is thus in the order of 1.2–1.4 eV. This large injection barrier prevents efficient charge injection and the hole current is low. Consequently OLEDs fabricated with gold as anode and barium as cathode exhibit a low, injection limited current and hardly any electroluminescence.[20]

The injection barrier at the anode, however, can be tuned by the ferroelectric polarization.[21] Figure 1b shows the diode when the ferroelectric is poled opposite to the electric field that drives the OLED. The negative polarization charge at the anode is compensated for by accumulated holes in the semiconducting PFO domains. The accumulated holes lead to strong band bending that lowers the injection barrier. The hole current becomes space charge limited.[21] Furthermore, the cathode contact remains Ohmic after polarization, so the diode is in the on-state and emits light. Similarly, Figure 1c shows that poling

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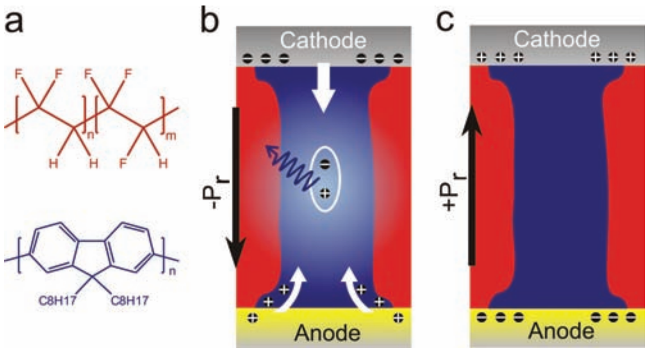

Figure 1. Overview of the MEMOLED operation mechanism using a phase separated blend of a ferroelectric polymer and a semiconducting polymer. a) Chemical structure of the ferroelectric random co-polymer P(VDF-TrFE) (blue) and the light-emitting semiconducting polymer PFO (red). b) MEMOLED poled in the on-state. When the ferroelectric is poled against the applied electric field, the polarization charge at the anode is compensated by holes in the PFO. Consequently, the injection barrier at the anode is lowered and the diode emits light. c) MEMOLED poled in the off-state. The ferroelectric is poled parallel to the applied electric field. The p-type semiconductor can not compensate the positive ferroelectric polarization. Hence, the anode becomes injection-limited, the hole current is completely suppressed and the MEMOLED is off.

in the opposite direction leads to an increase of the injection barrier. The hole current is completely suppressed, the diode is in the off-state and the light emission is negligible.

Experimentally, diodes were fabricated as presented in the experimental section. Tetrahydrofuran was used as common solvent. The spin-coated films were annealed at 140 °C to enhance the crystalline β-phase of P(VDF-TrFE) and hence the ferroelectricity.[22] We note that variation of the processing parameters such as drying rate, spinning speed and film thickness hardly changed the electrical and electroluminescent characteristics, demonstrating a large process window. It was verified that the electrical transport scaled with the device area, which was varied from 1 mm × 1 mm to 10 mm × 10 mm.

As a first step we determined the ferroelectric properties of P(VDF-TrFE). Measurements on pure P(VDF-TrFE) capacitors with a Sawyer-Tower circuit[23] showed a coercive field of 50 MV/m and a remnant polarization of 0.06–0.07 C m^{-2} in good agreement with literature data.[24] The remnant polarization of blend films could not directly be determined using Sawyer-Tower due to the parallel resistance of the PFO phase.[25] The remnant polarization of the 10% blend was measured with a pulse sequence procedure and amounted to approximately 90% of the pure P(VDF-TrFE) capacitors, i. e., ~0.05 C m^{-2}. Ferroelectricity in the blend was further proven by measuring the dielectric constant. The obtained butterfly shape for the dielectric constant as a function of electric field is a clear manifestation that polarization reversal is maintained in the blend.[17]

The current–voltage characteristic of a diode fabricated with a blend of PFO:P(VDF-TrFE) 10:90 (10% PFO) is presented in **Figure 2**a. Under forward bias the current shows bistability. At about 8 V, corresponding to the coercive field of P(VDF-TrFE) the diode switches from the high resistive off-state, governed by the trap-limited electron current in the PFO, to the low resistive on-state. The current in reverse bias is dominated by leakage which masks that at the corresponding bias of –8 V the diode is switched back from the on-state to the off-state. The corresponding light emission is presented in Figure 2b. In correspondence with the current also the light output is bistable and can be turned on and off with a voltage pulse that exceeds the coercive field. The diode in Figure 2 switches between an on-state and off-state at +8 V and –8 V respectively. At lower biases the non-volatile state is retained.

As stated above, the current in the forward bias of the Off-state is dominated by the trap limited electron current that starts at +3 V. However, the hole current switches on at the coercive field at around +8 V. Therefore in EL, we observe no light emission at fields lower than the coercive field. Light emission sets in at +8 V when the anode starts to inject holes. In the back sweep, the anode remains a good injecting contact for holes. Light emission is maintained down to +3 V, which corresponds to the onset of light emission of a PFO-only diode. The switching is due to the coercive field of the ferroelectric and therefore the yield of switching is unity. The spread in switching voltage is much less than 1 V.

The MEMOLED operates because the coercive field of the ferroelectric is larger than the electric field required to drive the light emission from the semiconductor. By applying high bias pulses, the resistance of the diode can be put into an on- or off-state. Since these states are non-volatile the diode in the on-state can be driven as a regular light emitting diode. We note that the luminance is presented in arbitrary units. The current density in the blend diode is comparable to that of a PFO-only diode. However, the light output is about one order of magnitude lower. Here we demonstrate the concept of the MEMOLED, the efficiency is not optimized yet.

The standard active matrix driving scheme for a display consisting of a word line, a bit line, a select- and a drive transistor and a storage capacitor is shown in **Figure 3**a. The pixel is addressed by the select transistor while the drive transistor regulates the actual light emission.[10] The storage capacitor is included to

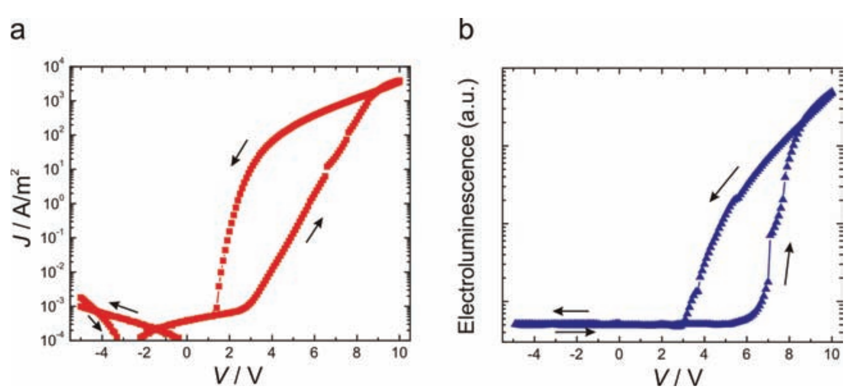

Figure 2. Opto-electrical characteristics of a MEMOLED fabricated with a PFO:P(VDF-TrFE) 10:90 blend. The diode is swept between +10 and –10 V, exceeding the coercive field. Hence the previous state of the device does not matter. a) The current voltage characteristics show electrical bistability due to the tunable hole injection barrier. b) The electroluminescence of the MEMOLED shows a corresponding hysteresis. Switching of the electroluminescence occurs above the coercive field of the ferroelectric.

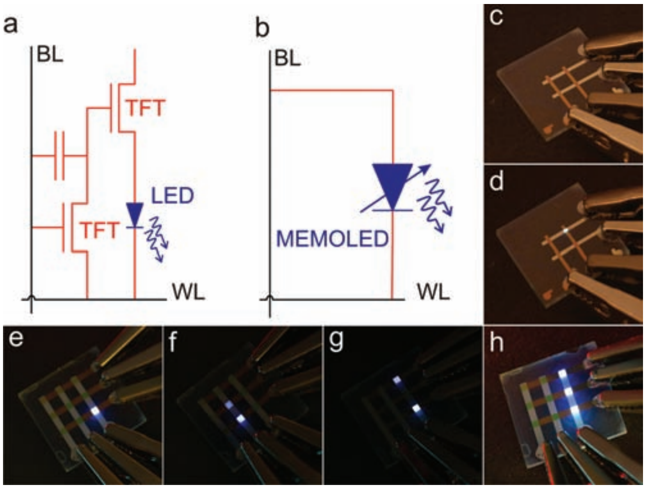

Figure 3. Active addressing with passive driving. a) Standard active matrix driving scheme. The pixel consists of a word line, a bit line, a select and a drive transistor and a storage capacitor as taken from Ref. [9]. b) The pixel layout in the MEMOLED concept; each pixel is actively addressed by the built-in ferroelectric switch and is driven passively. c) A 4-pixel display where all pixels are programmed in the off-state. d) the same display where one of the pixels is addressed. e–h) a 9-pixel display where different pixels are addressed.

maintain a constant voltage on the pixel over the entire frame cycle and to minimize the kick-back voltage resulting from the parasitic capacitance of the drive transistor.[10] Figure 3b shows the simple driving layout for a pixel in the MEMOLED concept, where only word- and bit lines are required. No select- or drive transistors are needed. Pixels are programmed into the desired on- and off-state by applying pulses above the coercive field of the ferroelectric. The non-volatile signage image is then generated by driving at lower biases. The elimination of cross-talk due to active addressing with the ferroelectric switch is also expected to lead to a reduction of the power efficiency as compared to conventional passive matrix displays, where the non-emitting pixels require a higher bias to prevent cross-talk. However, with the non-optimized MEMOLED a realistic comparison with conventional passive matrix displays is not possible yet. The uniqueness of the MEMOLED concept is that it combines the simple device architecture of a passive matrix display with active addressing by an integrated programmable switch.

A 4-pixel and a 9-pixel MEMOLED display are shown in Figure 3c–h. First in the 2 × 2 display of Figure 3c all the four pixels are set into the off-state. No light emission is observed when a bias is applied on the word line (WL) with the bit-line (BL) grounded. Then one pixel is addressed and programmed into the emissive on-state. To address this individual pixel an addressing voltage pulse, V_a, exceeding the coercive field of P(VDF-TrFE) is required. In order to prevent the disrupting effect of the addressing pulse on the state of the neighboring pixels, half the address voltage is applied on the word line and the other half on the bit-line. All other lines were grounded. In this way neighboring pixels experience a field below the coercive field and their state remains unaffected, as was also recently demonstrated in a memory matrix.[26] When applying a driving bias on all the word lines, as shown in Figure 3d, only the pixel that has been addressed in the on-state emits light. This unambiguously demonstrates the elimination of cross-talk. Discrete pixels can be put in the on and off-state without disturbing the emissive state of neighboring pixels. The same driving scheme was used to program and address the pixels in the 3 × 3 display. Figure 3e–h demonstrate that only the programmed pixels emit light and that the non addressed pixels remain in the non-emissive off-state.

Next to passive addressing also the switching time, cycle endurance and data retention of individual pixels are crucial parameters for any signage application. A typical MEMOLED with 10% PFO showed a switching time of less than 1 ms. The switching time is determined by the polarization switching of the P(VDF-TrFE), which is field dependent and can be reduced even further upon applying a higher switching bias.[24] The on- and off current as well as the corresponding electroluminescence show a small decrease upon 1000 repeated switching cycles, as presented in **Figure 4**. Whether this is due to degradation of the light-emitting polymer or fatigue of the ferroelectric phase is a subject of further study. The cycle endurance of the MEMOLED is comparable to that of organic non-volatile memories based on ferroelectric-semiconductor phase separated blends. In the present devices the measurement of the retention time is hampered by the deterioration of the barium cathode. We note, however, that upon encapsulation a similar long retention time

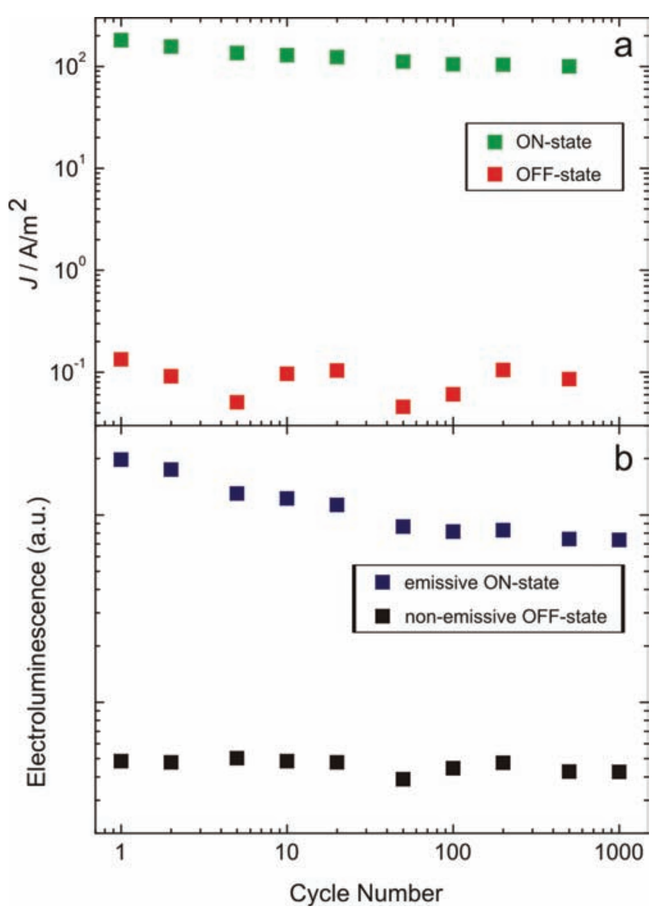

Figure 4. Cycle endurance of the MEMOLED. Pulses of ±20 V and 20 ms are used to program the device repeatedly into the on- and off-states. The current density and electroluminescence intensity was sampled at +5 V.

as ferroelectric capacitors can be expected.[27,28] Recently, we have demonstrated that the concept of a programmable injection barrier by ferroelectric polarization is widely applicable to a variety of organic semiconducting polymers with different emission colors.[21] These preliminary measurements therefore strengthen the viability of the MEMOLED for large area signage applications.

In summary, we have presented the MEMOLED. The concept is based on a tunable injection barrier, realized with a phase separated blend of a light-emitting and a ferroelectric polymer. The polarization field of the ferroelectric is used to modulate the injection barrier at the semiconductor–metal contact yielding an integrated on/off switch for light emission. A 2×2 and 3×3 display has been realized. Discrete pixels can be put in the on-state and off-state without disturbing the emissive state of neighboring pixels unambiguously demonstrating the elimination of cross-talk. The uniqueness of the MEMOLED concept is that it combines the simple device architecture of a passive matrix display with active addressing by an integrated programmable switch.

Experimental Section

The ferroelectric random copolymer (poly(vinylidene fluoride-*co*-trifluoroethylene)) (P(VDF-TrFE)) (80%–20%) was purchased from Solvay and poly(9,9-dioctylfluorenyl-2,7-diyl) end-capped with dimethylphenyl (PFO) was purchased from American Dye Source, Inc. Both materials were utilized as received. Pure P(VDF-TrFE) films were spin-coated from 30–50 mg mL^{-1} solutions in tetrahydrofuran (THF), dissolved at room temperature. Blend films were spin-coated from the P(VDF-TrFE) solution blended with an appropriate amounts of PFO, yielding a blending ratio of 10:90 PFO:P(VDF-TrFE). Solutions were filtered over 1 µm PTFE filters and processed in a nitrogen filled glove box. The films were spincoated onto a 15 nm semitransparent gold bottom electrode. A 1 nm chromium layer was used for adhesion. The blend films phase separate with bicontinuous domain of PFO embedded in a P(VDF-TrFE) matrix with a size of about 400 nm, as schematically depicted in Figure 1.[28] The spincoated films were annealed for two hours at 140 °C in vacuum oven in order to enhance the crystallinity of the P(VDF-TrFE) phase. The barium top electrode (15 nm) capped with aluminum (100 nm) was evaporated through a shadow mask. The dimension of the active area is varied from 1 mm × 1 mm to 10 mm × 10 mm. The ferroelectric polarization was characterized using a Sawyer-Tower circuit for the pure P(VDF-TrFE) capacitor. For blend diodes remanent polarization was measured using a positive up negative down pulse procedure with a Ferroelectric Test System (Radiant Technologies, INC.). The current-voltage and degradation measurements were conducted in a nitrogen filled glove box. To pole the diodes we applied 20 ms pulses of +10 V and –10 V, exceeding the coercive field. The current was read-out at a bias of +5 V. The morphology of the films was investigated with AFM and scanning transmission X-ray microscopy.

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[1] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, A. B. Holmes, *Nature* **1990**, *347*, 539.
[2] H. Sirringhaus, N. Tessler, R. H. Friend, *Science* **1998**, *280*, 1741.
[3] H. E. A. Huitema, G. H. Gelinck, J. B. P. H. Van Der Putten, K. E. Kuijk, C. M. Hart, E. Cantatore, P. T. Herwig, A. J. J. M. van Breemen, D. M. de Leeuw. *Nature* **2001**, *414*, 599.
[4] R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Brédas, M. Lögdlund, W. R. Salaneck, *Nature* **1999**, *397*, 121.
[5] H. Sirringhaus, P. J. Brown, R. H. Friend, M. M. Nielsen, K. Bechgaard, B. M. W. Langeveld-Voss, A. J. H. Spiering, R. A. J. Janssen, E. W. Meijer, P. Herwig, D. M. de Leeuw, *Nature* **1999**, *401*, 685.
[6] H. E. A. Huitema, G. H. Gelinck, J. B. P. H. Van Der Putten, K. E. Kuijk, C. M. Hart, E. Cantatore, D. M. de Leeuw, *Adv. Mater.* **2002**, *14*, 1201.
[7] M.-C. Choi, Y. Kim, C.-S. Ha, *Prog. Polym. Sci.* **2008**, *33*, 581.
[8] G. H. Gelinck, H. E. A. Huitema, E. Van Veenendaal, E. Cantatore, L. Schrijnemakers, J. B. P. H. Van Der Putten, T. C. T. Geuns, M. Beenhakkers, J. B. Giesbers, B. Huisman, E. J. Meijer, E. Mena Benito, F. J. Touwslager, A. W. Marsman, B. J. E. van Rens, D. M. de Leeuw, *Nat. Mater.* **2004**, *3*, 106.
[9] R. A. Street, *Adv. Mater.* **2009**, *21*, 2007.
[10] M. L. Chabinyc, A. Salleo, *Chem. Mater.* **2004**, *16*, 4509.
[11] E. L. Haskal, M. Buchel, P. C. Duineveld, A. Sempel, P. van de Weijer et al, *MRS Bull.* **2002**, *27*, 864.
[12] H. Kubota, S. Miyaguchi, S. Ishizuka, T. Wakimoto, J. Funaki, Y. Fukuda, T. Watanabe, H. Ochi, T. Sakamoto, T. Miyake, M. Tsuchida, I. Ohshita, T. Tohma, J. Lumin. **2000**, *87–9*, 56.
[13] A. Sempel, M. Buchel, *Org. Electron.* **2002**, *3*, 89.
[14] D. Braun, *Synthetic Metals* **1998**, *92*, 107.
[15] A. J. Campbell, D. D. C. Bradley, H. Antoniadis, *J. Appl. Phys.* **2001**, *89*, 3343.
[16] L. S. Liao, C. S. Lee, S. T. Lee, M. Inbasekaran, W. W. Wu, *Conjugated Polymer and Molecular Interfaces*, (Eds: SW. R. Salaneck, A. Seki, A. Kahn, J.-J. Pireaux), Marcel Dekker New York **2000.**
[17] K. Asadi, D. M. de Leeuw, B. de Boer, P. W. M. Blom, *Nat. Mater.* **2008**, *7*, 547.
[18] T. Van Woudenberg, J. Wildeman, P. W. M. Blom, J. J. A. M. Bastiaansen, B. M. W. Langeveld-Voss, *Adv. Funt. Mater.* **2004**, *14*, 677.
[19] T. M. Brown, R. H. Friend, I. S. Millard, D. J. Lacey, T. Butler, J. H. Burroughes, F. Cacialli, *J. Appl. Phys.* **2003**, *93*, 6159.
[20] T. Van Woudenberg, P. W. M. Blom, J. N. Huiberts, *Appl. Phys. Lett.* **2003**, *82*, 985.
[21] K. Asadi, T. G. de Boer, P. W. M. Blom, D. M. de Leeuw, *Adv. Funct. Mater.* **2009**, *19*, 3173.
[22] H. Kodama, Y. Takahashi, T. Furukawa, *Ferroelectrics* **1997**, *203*, 433.
[23] C. B. Sawyer, C. H. Tower, *Phys. Rev.* **1930**, *35*, 269.
[24] T. Furukawa, *Adv. Colloid interface Sci.* **1997**, *71–2*, 183.
[25] J. F. Scott, *J. Phys. Condens. Mat.* **2008**, *20*, 021001.
[26] K. Asadi, M. Li, N. Stingelin, P. W. M. Blom, D. M. de Leeuw, *Appl. Phys. Lett.* **2010**, *97*, 193308.
[27] J. F. Scott, *Ferroelectric Memories*, Springer, Heidelberg, **2000**.
[28] C. R. McNeill, K. Asadi, B. Watts, P. W. M. Blom, D. M. de Leeuw, *Small* **2010**, *6*, 508.
[29] K. Asadi, J. Wildeman, P. W. M. Blom, D. M. de Leeuw, *IEEE T Electron. Dev.* **2010**, *57*, 3466.